Carbonation of Filler Type Self-compacting Concrete

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1. Introduction

Self-compacting concrete (SCC) is a new kind of concrete that combines a high flowability and a high segregation resistance obtained by a large amount of fine particles and the use of superplasticizers. Due to the presence of the large amount of fine particles, the pore structure is somewhat different from the pore structure of traditional concrete. Because the pore structure is one of the major influencing factors concerning durability, the actual application of SCC might be somewhat risky due to the lack of knowledge concerning the actual durability of the new cementitious material. Significant research programmes have already been carried out concerning the fresh properties of SCC, but only few information is known about the durability of SCC.

The durability is not like strength a bulk property but in the first place a surface property. The concrete surface differs from the inner concrete due to the wall effect, sedimentation and segregation. Therefore, the surface layer determines the ease with which fluids and gases can enter into and move through the concrete, thus influencing the service life of the concrete structure.

The concrete cover generally provides protection against corrosion of steel due to its highly alkaline nature. This alkalinity corresponds to a pH value somewhat larger than 12.5 and is provided by the dissolution in the pore water of a very small amount of the solid $Ca(OH)_2$ in the hardened cement gel. The dissolved $Ca(OH)_2$ in the pore water and the solid $Ca(OH)_2$ in the cement gel is converted to $CaCO_3$ due to the reaction with the atmospheric CO_2, causing a loss of alkalinity. This process of conversion of calcium hydroxide to calcium carbonate is termed carbonation. Depassivation of the steel occurs if the pH value of the pore water is reduced below 9. If the carbonation front reaches the steel, the latter will depassivate and corrode afterwards in the presence of moisture and oxygen.

In order to study the carbonation behaviour of self-compacting concrete, concrete cubes were made of 16 SCC mixtures and 4 traditional concrete mixtures. Four types of cement (portland cement and blast furnace slag cement), three types of filler (fly ash and two types of limestone filler with a different grading curve) and two types of coarse aggregate are used and the influence of the amount of powder (cement and filler material) and the amount of water is studied. These concrete cubes were stored

permanently in a carbonation room at 20°C, 60% R.H. and 10% CO_2. At certain times, the carbonation depth is determined with phenolphthalein and the carbonation coefficient is determined.

The main influencing factors in the carbonation process are the diffusion of CO_2 into the concrete and the amount of hydrated cement reacting with the CO_2. These two parameters could be determined based on the concrete composition, degree of hydration and the chemical composition of the cement.

In the last part of the paper, the calculated and experimental carbonation coefficient are compared.

2. Experimental programme

2.1 Mixture design

At the Magnel Laboratory for Concrete Research, 16 self-compacting concrete mixtures (SCC) and 4 traditional concrete mixtures (TC) were investigated.

Table 1: Mixture Composition

	CEM I 42.5 R [kg/m³]	CEM I 52.5 [kg/m³]	CEM III A 42.5 LA [kg/m³]	CEM I 52.5 HSR [kg/m³]	limestone filler S [kg/m³]	limestone filler P2 [kg/m³]	fly ash [kg/m³]	water [kg/m³]	sand 0/5 [kg/m³]	gravel 4/14 [kg/m³]	Limestone gravel 2/14 [kg/m³]	W/C [-]	C/P [-]	compr. strength [MPa]
SCC1	360					240		165	853	698		0.46	0.60	57.3
SCC2		360				240		165	853	698		0.46	0.60	68.0
SCC3			360			240		165	853	698		0.46	0.60	66.1
SCC4				360		240		165	853	698		0.46	0.60	70.1
SCC5	300					300		165	853	698		0.55	0.50	46.5
SCC6	400					200		165	853	698		0.41	0.67	64.2
SCC7	450					150		165	853	698		0.37	0.75	68.7
SCC8	360				240			165	853	698		0.46	0.60	56.9
SCC9	360						240	165	853	698		0.46	0.60	66.2
SCC10	300					200		137	923	755		0.46	0.60	60.1
SCC11	400					300		192	782	640		0.48	0.57	55.9
SCC12	450					350		220	712	583		0.49	0.56	50.9
SCC13	360					240		144	865	707		0.40	0.60	68.7
SCC14	360					240		198	835	683		0.55	0.60	46.6
SCC15	360					240		216	825	675		0.60	0.60	40.3
SCC16	360					240		165	816		734	0.46	0.60	74.7
TC1	360							165	640	1225		0.46	1.00	48.6
TC2			360					165	640	1225		0.46	1.00	49.7
TC3				360				165	640	1225		0.46	1.00	50.2
TC4	400							165	640	1220		0.41	1.00	53.7

In the first 9 mixtures a constant amount of cementitious materials (cement and filler) is considered: 600kg/m³, as well as a constant amount of water, sand and gravel, respectively 165k/m³, 853 kg/m³ and 698 kg/m³. Four types of cement are used (Portland cement CEM I 42.5 R, CEM I 52.5, CEM I 52.5 HSR and blast furnace slag cement CEM III A 42.5 LA), three types of filler (fly ash and two types of limestone filler BETOCARB P2 and Superfine S, the last one having a finer grading). In the next three mixtures, the amount of powder is varied (500 kg/m³, 700 kg/m³ and 800 kg/m³). In the following three mixtures, the amount of water is varied (144 kg/m³, 198 kg/m³ and 216 kg/m³). In SCC16 crushed limestone gravel was used instead of river gravel.

For the traditional concrete mixtures, the type of cement is varied in the first three mixtures with the same water/cement ratio as for SCC1. For TC4 a lower water/cement ratio is used.

The amount of superplasticizer, which is a modified polycarboxylether, was determined in order to obtain a suitable flowability without segregation. Also the flowing time in the V-funnel was measured (values between 5s and 10s), air content (values between 1% and 3%) and the U-box requiring self-levelling. In table 1 the mixture composition is given together with the compressive strength at 28 days measured on concrete cubes with side 150mm, the water/cement ratio (W/C) and the cement/powder ratio (C/P).

2.2 Test method

From the mixes described above, cubes 100 x 100 x 100mm³ were made. These concrete cubes were stored in a climate chamber at 20°C $\pm$ 2 °C and more than 90% R.H.. At the age of 28 days, an epoxy coating was applied to all surfaces, except on the surface exposed to CO_2. The concrete cubes were stored permanently in a carbonation room at 20°C, 60% R.H. and 10 vol.% CO_2. At regular times (8, 12, 16, 20, 24 and 28 weeks) the carbonation depth was examined experimentally. At each time, a slice with a thickness of 1 cm was sawn from each specimen. This slice was sprayed with a phenolphthalein solution in order to determine the carbonated zone. This pH indicator changes from colourless to purple as the pH rises from 8.3 to 10.0. The test indicates the depth to which the calciumhydroxide has been depleted. After the sawing of the slices, the remaining concrete specimen was covered again with the carbondioxide resisting epoxy coating and the treatment was continued.

2.3 Experimental results

The carbonation of concrete can be considered as a Fickian problem because it is a diffusion controlled process. This process is governed by the equation:

$$x = A\sqrt{t} \tag{1}$$

in which x is the carbonation depth (mm), t is the exposure time (year) and A a constant depending on the diffusion resistance of the material (mm/√year). In literature, most of the models are following this law, although some other models can be found.
After sawing a slice of the concrete cube, the carbonation depth is determined at 10 points and the mean value is calculated. For each composition, at least three concrete cubes are made in order to obtain a mean carbonation depth. With the carbonation depths at several times, and with equation (1), a regression value for the parameter A can be determined. The resulting A-values are given in table 2 together with the number of cubes tested for each mixture.

Table 2: Values for A (experimental conditions) and number of test specimens N

	A [mm/√year]	N
SCC1	14.4	5
SCC2	10.9	5
SCC3	23.3	3
SCC4	14.6	5
SCC5	23.0	5
SCC6	11.0	5
SCC7	7.5	8
SCC8	14.1	5
SCC9	14.2	5
SCC10	11.1	6
SCC11	16.6	6
SCC12	17.6	3
SCC13	12.0	6
SCC14	31.2	6
SCC15	32.2	3
SCC16	7.5	3
TC1	11.5	5
TC2	25.7	3
TC3	3.7	5
TC4	4.2	5

From these results, the following observations can be made, taking SCC1 as reference concrete:

- cement type: a cement type with a higher strength (SCC2), resulting in a higher concrete strength (using the same W/C-ratio), leads to a lower carbonation depth.
  A blast furnace slag cement (SCC3) gives a higher penetration depth than Portland cement (SCC1). Also for traditional concrete, with TC1 as reference, the use of blast furnace slag cement in TC2 leads to an increase of the penetration depth.
  High sulphate resistant cement (SCC4) has a lower C_3A content and a higher C_2S and C_3S content, leading to an increased amount of $Ca(OH)_2$ and CSH and a lower penetration depth. This effect is more pronounced for traditional concrete (TC3 compared to TC1) than for self-compacting concrete (SCC4 compared to SCC1).
- W/C ratio: with a constant powder and water content and a varying amount of cement, the water cement ratio is varied (0.37 for SCC7, 0.41 for SCC6, 0.46 for SCC1 and 0.55 for SCC5). In this way, the compressive strength is also influenced (respectively 46, 56, 64 and 69 N/mm²). A lower W/C-ratio and a higher strength result in a lower carbonation depth. Moreover, by the increased amount of cement, the amount of $Ca(OH)_2$ and CSH will increase, resulting in a higher amount of bounded CO_2 and a lower penetration depth.
- type of filler: the use of a limestone filler with a finer grading does not change the carbonation depth (SCC8 versus SCC1).
  The use of fly ash (SCC9) gives a higher strength and a denser pore structure, yielding a lower penetration depth. But, in the same time, part of the $Ca(OH)_2$ is consumed by the hydration of the fly ash, leading to a higher penetration depth. The result, in this case, is that the carbonation coefficient remains almost constant.
- amount of powder: increasing the amount of powder with a constant C/P ratio and a constant W/C ratio, leads to an increase in the amount of paste. This increase in paste creates an increase in the total porosity, leading to a higher carbonation coefficient.
- amount of water: increasing the amount of water (increasing the W/C ratio and decreasing the strength) results in a higher penetration depth (SCC13: 144 kg/m³, SCC1: 165 kg/m³, SCC14: 198 kg/m³ and SCC15: 216 kg/m³).
- type of coarse aggregate: by replacing the river gravel by crushed aggregate, the bonding between the paste and the aggregate will be better. This leads to a decrease of the carbonation depth. The test result shows a stronger decrease than what could be expected.
- TC in comparison with SCC: TC gives lower values for the penetration depth than the corresponding SCC (TC1 - SCC1; TC3 - SCC4 and TC4 - SCC6), although the traditional concrete has a lower compressive strength. This is not the case for TC2 – SCC3.

3.0 Modelling

3.1 Introduction

From the Fickian law and the work of Schröder [1,2], the carbonation coefficient could be written as:

$$A = \sqrt{2\frac{D}{a}(c_1 - c_2)} \tag{2}$$

with D the diffusion coefficient of the penetrating CO_2 into the concrete (m²/s), a the amount of carbonatable material (mol CO_2/m³ concrete) and c_1-c_2 the concentration difference between the outside environment and the uncarbonated concrete (mol/m³).
In literature [2,3,4,5], the diffusion of a gas, e.g. CO_2, through concrete is often written in function of the capillary porosity φ (-). In this paper, the following relation, given in equation (3) is used. The power 1.8 is also used in [2,3,4].

$$D \sim \varphi^{1.8} \tag{3}$$

For the determination of the amount of carbonatable material, different approaches are given in literature [5,6,7]. In this paper, the approach of Papadakis et al. [7] will be followed. This approach is starting from the chemical composition of the cement as will be explained in section 3.3.

3.2 Calculation of capillary porosity

In literature, it is written that the transport properties of concrete are mainly determined by capillary pores [8,9]. Therefore, the model of Powers et al. [10] is used to determine the capillary porosity.

$$V_{cap} = \text{capillary pores} + \text{free water} = \text{capillary pores} + \text{water} - \text{gel water} - \text{bounded water}$$

$$= 0.185\frac{Ch}{\rho_c} + \frac{W}{\rho_w} - \frac{0.28}{0.72}\left(\frac{Ch}{\rho_c}(1-0.185) + \frac{0.23\,Ch}{\rho_w}\right) - \frac{0.23\,Ch}{\rho_w} \tag{4}$$

$$= -0.1319\frac{Ch}{\rho_c} + \frac{1}{\rho_w}(W - 0.3194\,Ch)$$

with V_{cap} the volume of capillary pores [m³], C the amount of cement [kg], W the amount of water [kg], h the degree of hydration [-], ρ_c and ρ_w the mass density of respectively cement and water [kg/m³].

$$V_{concrete} = V_{water} + V_{cement} + V_{coarse\ aggregate} + V_{sand} + V_{filler}$$

$$= \frac{W}{r_w} + \frac{C}{r_c} + \frac{A+S+F}{r_{agg}} \qquad (5)$$

$$capillary\ porosity = \frac{V_{cap}}{V_{concrete}} \qquad (6)$$

with $V_{concrete}$ the volume [m³], A the amount of coarse aggregate [kg], S the amount of sand [kg], F the amount of filler [kg] and ρ_{agg} the mass density of aggregate [kg/m³].

The parameters W, C, A, S and F are known from the mixture proportions. For the mass densities, a value of 1000 kg/m³ is used for water, 2625 kg/m³ for the aggregates, sand and filler and 3115 kg/m³ for portland cement.

The test specimens are stored until the testing age in a climate room at 20°C ± 2 °C and at least 90% R.H. for at least 28 days. This means that the degree of hydration will not strongly differ from the ultimate degree of hydration, which could be determined by the Mill formula:

$$h_{ultim} = \frac{1.031\ {}^{W}\!/\!{}_{C}}{0.194 + {}^{W}\!/\!{}_{C}} \qquad (7)$$

3.3 Calculation of amount of carbonatable material

Papadakis et al. [7] propose that a is equal to the total molar concentration of CaO in the carbonatable constituents of the concrete:

$$a = [Ca(OH)_2] + 3[CSH] + 3[C_3S] + 2[C_2S] \qquad (8)$$

These molar concentrations should be determined at the moment the carbonation starts and should be expressed in mol/m³. The amount of C_3S and C_2S was determined for the Portland cements and is given in table 3, together with the chemical composition of the cements. By using the ultimate degree of hydration, the amount of CSH and $Ca(OH)_2$ could be determined based on the chemical hydration reactions.

For the mixtures with blast furnace slag cement and with fly ash, this approach could not be used. Those mixtures will not be modelled (SCC3, SCC9 and TC2).

Table 3: Chemical composition of cement

	CEM I 42.5 R	CEM I 52.5	CEM I 52.5 HSR
SiO_2 (%)	19.6	20.3	20.8
Al_2O_3 (%)	5.0	4.5	3.6
Fe_2O_3 (%)	3.0	2.3	3.9
CaO (total) (%)	61.5	64.0	64.2
MgO (%)	0.8	2.2	2.4
SO_3 (%)	3.3	3.3	2.7
Na_2O (%)	0.4	0.2	0.2
K_2O (%)	0.9	0.9	0.5
C_3S (%)	58.2	59.0	60.6
C_2S (%)	12.7	12.6	16.6
C_3A (%)	8.2	8.0	2.7
C_4AF (%)	9.1	9.4	13.1

3.4 Modelling results

Because D is proportional to the capillary porosity (eq. 3) and c_1-c_2 is a constant, the following relation is obtained from equation 2:

$$A \sim \sqrt{\frac{\varphi^{1.8}}{a}} \qquad (9)$$

In table 4, the values of the capillary porosity φ, the amount of carbonatable material a and $\sqrt{\frac{\varphi^{1.8}}{a}}$ are given.

In figure 1, the experimental value of the carbonation coefficient A is plotted in function of $\sqrt{\frac{\varphi^{1.8}}{a}}$ for each mixture. A good correlation (R^2 = 0.88) is obtained. The mixtures TC3 and TC4 are not giving a good correlation. This could be explained by the large scatter in the results for traditional concrete (the values for TC2 being very high and for TC3 and TC4 very low, see table 2). This large scatter, as explained in [2], is mainly due to the vibration with a needle of the test specimens. These were concrete cubes with side 100mm. The vibration could have caused some segregation and a more porous trowelled face. It was this face that was exposed to CO_2.

Table 4: Calculation of $\sqrt{\dfrac{\varphi^{1.8}}{a}}$

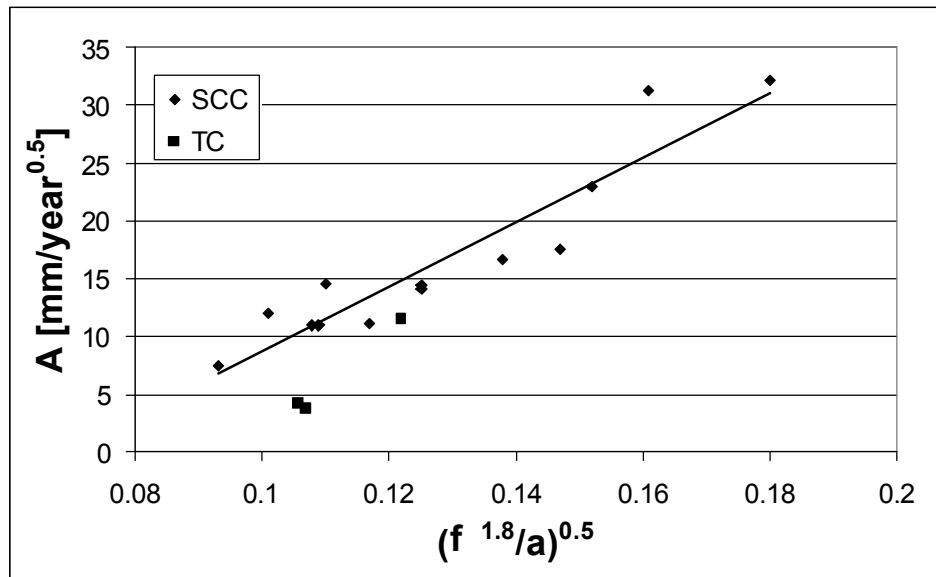|	φ (%)	a (mol CO_2/m³ concrete)	$\sqrt{(\varphi^{1.8}/a)}$
SCC 1	7.33	2311	0.125
SCC 2	6.72	2648	0.108
SCC 4	6.73	2566	0.110
SCC 5	7.33	2311	0.125
SCC 7	8.51	2032	0.152
SCC 8	6.61	2496	0.109
SCC 9	5.76	2688	0.093
SCC 10	6.16	1925	0.117
SCC 11	8.78	2603	0.138
SCC 12	10.07	2968	0.147
SCC 13	5.63	2214	0.101
SCC 14	10.03	2439	0.161
SCC 15	11.51	2503	0.180
SCC 16	7.33	2311	0.125
TC 1	7.11	2311	0.122
TC 3	6.53	2566	0.107
TC 4	6.41	2496	0.106

Figure 1: Modelling of the carbonation coefficient A

4. Conclusions

In this article, the carbonation of 16 self-compacting concrete mixtures and of 4 traditional concrete mixtures is discussed. The selection of the mixtures is made in order to consider some important parameters like the type of cement (Portland cement of two different strength classes, blast furnace slag cement and a high sulphate resisting cement), type of filler (fly ash and limestone filler with two different grading curves), the cement/powder and water/cement ratio, the amount of water, the amount of powder (cement and filler) and the type of coarse aggregate. The results of these tests are discussed and a model is proposed. The following conclusions could be made:
- the carbonation of concrete is influenced by the diffusion of CO_2 through the concrete and by the amount of carbonatable material present in the concrete. The diffusion coefficient is mainly determined by the capillary porosity. The amount of carbonatable material depends on the type of cement, the cement content and the degree of hydration
- The type of cement is a main influencing factor, both for traditional and self-compacting concrete.
- The use of limestone filler with a finer grading curve does almost not influence the carbonation behaviour.
- The use of fly ash as filler material decreases the porosity and decreases the amount of carbonatable material. Both effects are in equilibrium in the investigated mixture, leading to a very comparable carbonation coefficient regarding the reference mixture.
- The decrease of the capillary porosity, obtained by e.g. a lower W/C ratio, a higher C/P ratio, a lower water content,..., decreases the carbonation rate.

5. References

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